

Appendix F

Dechlorination Memorandum

Review of Natural PCB Degradation Processes in Sediments for the Lower Fox River and Green Bay, Wisconsin

Prepared for:

Wisconsin Dept. of Natural Resources



◆ **The RETEC Group, Inc.**

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Review of Natural PCB Degradation Processes in Sediments

Prepared by:

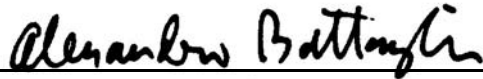
The RETEC Group, Inc.
3040 William Pitt Way
Pittsburgh, Pennsylvania 15238

RETEC Project No.: WISCN-14414-530

Prepared for:

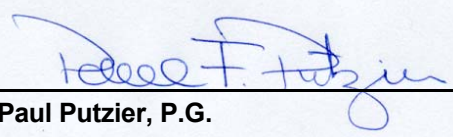
Wisconsin Department of Natural Resources
101 South Webster Street
Madison, Wisconsin 53707

Prepared by:



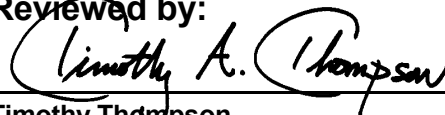
Alessandro Battaglia, Ph.D., P.E.

Project Manager:



Paul Putzier, P.G.

Reviewed by:



Timothy Thompson

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1 Introduction

This paper provides a review of literature documenting field and laboratory studies that examine the occurrence and extent of natural biodegradation processes (aerobic degradation and anaerobic dechlorination) of polychlorinated biphenyls (PCBs) at various sites both in the U.S and internationally. The review was prepared as part of the Lower Fox River Remedial Investigation/Feasibility Study.

The objective of this review was to evaluate information relating to the viability of natural biodegradation as a potential remedial action for the sediment-bound PCBs in the Lower Fox River and Green Bay. The information presented in this paper will be evaluated together with additional site-specific information generated for the Lower Fox River and Green Bay in the Feasibility Study. It is recognized that the rate at which *in situ* microbial processes can occur is an important element of any evaluation of such processes when assessing natural bioremediation as a potential remedial action. However, based on the results of the literature review presented here, no degradation (aerobic or anaerobic) rates have been reliably measured under field conditions. The only rates that have been estimated are for laboratory experiments done under controlled conditions. These rates are generally not applicable to field conditions; as such, they are not reported in this paper.

The paper consists of five sections, in addition to this introductory section, articulated as follows.

- Section 2 provides an overview of PCB chemistry and nomenclature;
- Section 3 provides a review of microbial processes relevant to PCBs;
- Section 4 provides a review of field and laboratory studies of natural degradation of PCBs in sediments;
- Section 5 provides the conclusion of the literature review; and
- Section 6 is a list of cited references.

2 PCB Chemistry, Nomenclature, and Toxicology

PCBs are a class of 209 individual chemicals (PCB congeners), in which one to ten chlorine atoms are attached to a biphenyl molecular frame. PCBs were commercially produced as mixtures for a variety of uses, including dielectric fluids in capacitors and transformers, and carbonless copy paper. Monsanto Industrial Chemicals Company (Monsanto) was the world's largest producer and sole manufacturer of commercial PCBs in the U.S. Monsanto marketed PCBs under the trade name Aroclor from 1930 to 1977 (Erickson 1986). Table 2-1 provides a list of the uses of PCBs and the type of Aroclor used.

Most Aroclors contained from 60 to 90 different PCB congeners and were identified by a four-digit number; the first two digits were usually 12, for 12 carbon atoms, and the last two digits indicated the percent substituted chlorine by weight. Thus, Aroclor 1242 contains 12 carbon atoms and 42% substituted chlorine by weight (Hutzinger *et al.*, 1974; Bedard and Quensen 1995). Table 2-2 provides the chlorine content of various Aroclors.

Key to the discussion of natural degradation processes is an understanding of the nomenclature associated with the numbering and position of the chlorine atoms within the PCB biphenyl rings. The general chemical formula for PCBs is



with n indicating the number of chlorine substitutions; $n=1$ through 10.

PCB congeners with the same number of chlorine substitutions are defined as a class of PCB homologs. For example, the twenty-four PCB congeners with three chlorine substitutions form the trichlorobiphenyl homolog class. PCB congeners in a given homolog class are sometimes referred to as PCB isomers (Erickson, 1986).

The chlorine positions on the biphenyl rings are numbered as shown in Figure 2-1(a). Different congeners are specified by the positions of the chlorine atoms. For example, in Figure 2-1(b), the 2,4'-dichlorobiphenyl is shown. (As discussed later, this is the most abundant congener in Aroclor 1242). PCB congeners have been arranged in ascending numerical order between 0 (biphenyl) and 209 (2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl) and are commonly identified by this number, which is referred to as the "IUPAC" or "PCB" number. For example, the 2,4' dichlorobiphenyl congener is also referred to as PCB 8. Finally, some authors refer to individual congeners by listing the substituted positions on each ring,

separated by a hyphen. Thus, in this notation 2,4' dichlorobiphenyl is referred to as 2-4 chlorobiphenyl or 2-4-CB. This paper reports on studies by a number of authors. To minimize the possibility of transcription errors, the notation used by each author is used when reporting on that author's results.

As shown in Figure 2-1(c), chlorine atoms at positions 2, 6, 2' and 6' are referred to as being oriented *ortho* with respect to the opposite phenyl ring. Positions 3, 5, 3' and 5' are oriented *meta*, while positions 4 and 4' are oriented *para* with respect to the opposite phenyl ring.

Table 2-1 Uses of PCBs (from Huntzinger *et al.*, 1974)

Use of PCB	Grade of Aroclor Used
Electrical capacitors	1016 (1221, 1254)
Electrical transformers	1242, 1254, 1260
Vacuum pumps	1248, 1254
Gas-transmission turbines	1221, 1242
Hydraulic fluids	1232, 1242, 1248, 1254, 1260
Plasticizer in synthetic resins	1248, 1254, 1260, 1262, 1268
Adhesives	1221, 1232, 1242, 1248, 1254
Plasticizer in rubbers	1221, 1232, 1242, 1248, 1254, 1268
Heat transfer systems	1242
Wax extenders	1242, 1254, 1268
Dedusting agents	1254, 1260
Pesticide extenders, inks, lubricants, cutting oils	1254
Carbonless reproducing paper	1242

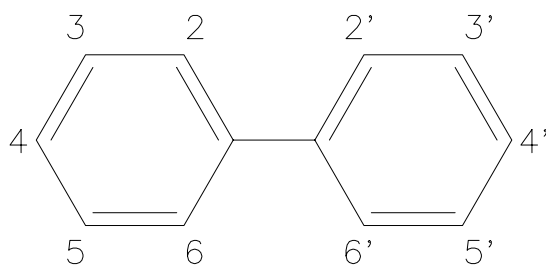
Table 2-2 Chlorine Content of Aroclor Preparations

Aroclor	% Cl	Average number of Cl per molecule	Average molecular weight
1221	20.5 – 21.5	1.15	192
1232	31.5 – 32.5	2.04	221
1242	42	3.10	261
1248	48	3.90	288
1254	54	4.96	327
1260	60	6.30	372
1262	61.5 – 62.5	6.80	389
1268	68	8.70	453

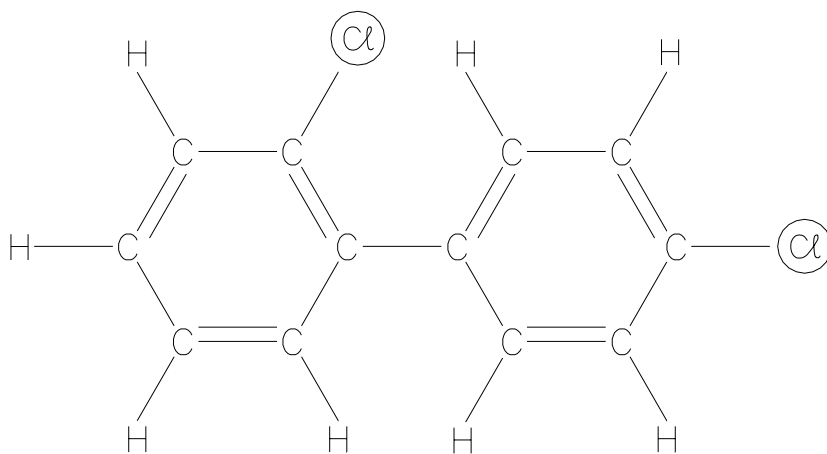
Selected physical and chemical properties of PCB congeners are presented in Tables 2-3 and 2-4. Table 2-5 presents the molecular composition of some Aroclors. This table shows that Aroclor 1242 is mostly comprised of tri-, tetra- and pentachlorobiphenyls, and that no congeners with more than six chlorine substitutions are present in Aroclor 1242.

Figure 2-1 PCB Structure and Nomenclature

a) Numbering in the Biphenyl Ring System



b) Structure of 2,4'-dichlorobiphenyl



c) Orientation of Chlorine Atoms in Biphenyl Ring System

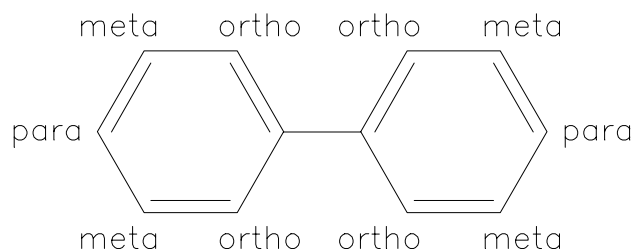


Table 2-3 Summary of Physical-Chemical Properties of PCB Congeners

Number	Structure	Molecular Weight	Solid Vapor Pressure P^s Pa	Subcooled Liquid Vapor Pressure P_L Pa	Water Solubility S g/m ³	Solid Molar Concentration C^s mmol/m ³	Subcooled Liquid Concentration C_L mmol/m ³	Log K_{ow}	Henry's Law Const. H Pa m ³ /mol
0	0	154.21	1.3	3.69	7	45.39	129.7	3.9	53.5
1	2	188.66	2.04	2.5	5.5	29.15	35.66	4.3	70.1
2	3	188.66	1	1	2.5	13.25	13.24	4.6	75.55
3	4	188.66	0.271	0.9	1.2	6.36	21.15	4.5	42.56
4	2,2'	223.11	0.265	0.6	1	4.48	10.14	4.9	59.17
5	2,3	223.11							
6	2,3'	223.11							
7	2,4	223.11	0.254	0.25	1.25	5.6	5.51	5	45.39
8	2,4'	223.11			1	4.48	6.73	5.1	
9	2,5	223.11	0.18	0.18	2	8.96	8.95	5.1	20.1
10	2,6	223.11			1.4	6.28	7.84	5	
11	3,3'	223.11	0.027	0.03	0.354	1.587	1.738	5.3	17.26
12	3,4	223.11			0.008				
13	3,4'	223.11							
14	3,5	223.11	0.105	0.12					
15	4,4'	223.11	0.0048	0.08	0.06	0.269	4.56	5.3	17
16	2,2',3	257.56							
17	2,2',4	257.56							
18	2,2',5	257.56	0.143	0.22	0.4	1.55	2.39	5.6	92.21
19	2,2',6	257.56							
20	2,3,3'	257.56							
21	2,3,4	257.56							
22	2,3,4'	257.56							
23	2,3,5	257.56							
24	2,3,6	257.56							
25	2,3',4	257.56							
26	2,3',5	257.56			0.251	0.975	1.387		

Table 2-3 Summary of Physical-Chemical Properties of PCB Congeners (Continued)

Number	Structure	Molecular Weight	Solid Vapor Pressure P^s Pa	Subcooled Liquid Vapor Pressure P_L Pa	Water Solubility S g/m ³	Solid Molar Concentration C^s mmol/m ³	Subcooled Liquid Concentration C_L mmol/m ³	Log K_{ow}	Henry's Law Const. H Pa m ³ /mol
27	2,3',6	257.56							
28	2,4,4'	257.56			0.16	0.621	1.28	5.8	
29	2,4,5	257.56	0.132	0.044	0.14	0.544	1.81	5.6	24.29
30	2,4,6		0.0384	0.09	0.2	0.777	1.82	5.5	49.51
31	2,4',5	257.56							
32	2,4',6	257.56							
33	2,3,4	257.56	0.0136	0.003	0.08	0.311	0.69	5.8	43.67
34	2',3,5	257.56							
35	3,3',4	257.56							
36	3,3',5	257.56							
37	3,4,4'	257.56			0.015	0.0582	0.24	5.9	
38	3,4,5	257.56							
39	3,4',5	257.56							
40	2,2',3,3'	292.01	0.00225	0.002	0.03	0.103	0.91	5.6	21.94
41	2,2',3,4	292.01							
42	2,2',3,4'	292.01							
43	2,2',3,5	292.01							
44	2,2',3,5'	292.01			0.1	0.342	0.565	6	
45	2,2',3,6	292.01							
46	2,2',3,6'	292.01							
47	2,2',4,4'	292.01	0.0054	0.002	0.09	0.308	1.15	5.9	17.38
48	2,2',4,5	292.01							
49	2,2',4,5'	292.01			0.016	0.0548	0.133	6.1	
50	2,2',4,6	292.01							
51	2,2',4,6'	292.01							
52	2,2',5,5'	292.01	0.0049	0.002	0.03	0.103	0.42	6.1	47.59
53	2,2,5,6'	292.01						5.5	
54	2,2',5,6'	292.01						5.48	

Table 2-3 Summary of Physical-Chemical Properties of PCB Congeners (Continued)

Number	Structure	Molecular Weight	Solid Vapor Pressure P^s Pa	Subcooled Liquid Vapor Pressure P_L Pa	Water Solubility S g/m ³	Solid Molar Concentration C^s mmol/m ³	Subcooled Liquid Concentration C_L mmol/m ³	Log K_{ow}	Henry's Law Const. H Pa m ³ /mol
55	2,3,3',4	292.01							
56	2,3,3',4'	292.01							
57	2,3,3',5	292.01							
58	2,3,3',5'	292.01							
59	2,3,3',6	292.01							
60	2,3,4,4'	292.01						6.31	
61	2,3,4,5	292.01			0.02	0.0685	0.314	5.9	
62	2,3,4,6	292.01							
63	2,3,4',5	292.01							
64	2,3,4',6	292.01							
65	2,3',4,4'	292.01						5.94	
66	2,3',4,4'	292.01			0.04	0.0147	1.3	5.8	
67	2,3',4,5	292.01							
68	2,3',4,5'	292.01							
69	2,3',4,6	292.01							
70	2,3',4',5	292.01							
71	2,3',4',6	292.01							
72	2,3',5,5'	292.01							
73	2,3',5',6	292.01							
74	2,4,4',5	292.01							
75	2,4,4',6	292.01			0.091			6.21	
76	2',3,4,5	292.01							
77	3,3',4,4'	292.01	0.0000588	0.002	0.001	0.0342	1.165	6.5	1.72
78	3,3',4,5	292.01							
79	3,3',4,5'	292.01							
80	3,3',5,5'	292.01			0.0012	0.0041	0.0974		
81	3,4,4',5	292.01							
82	2,2',3,3',4	326.46							
83	2,2',3,3',5	326.46							

Table 2-3 Summary of Physical-Chemical Properties of PCB Congeners (Continued)

Number	Structure	Molecular Weight	Solid Vapor Pressure P^s Pa	Subcooled Liquid Vapor Pressure P_L Pa	Water Solubility S g/m ³	Solid Molar Concentration C^s mmol/m ³	Subcooled Liquid Concentration C_L mmol/m ³	Log K_{ow}	Henry's Law Const. H Pa m ³ /mol
84	2,2',3,3',6	326.46	0.00927 0.000304	0.051 0.0023	0.02 0.004 0.012	0.0613 0.0123 0.0368	0.337 0.0927 0.202	6.2 6.5 6.5	151.4 24.81
85	2,2',3,4,4'	326.46							
86	2,2',3,4,5	326.46							
87	2,2',3,4,5'	326.46							
88	2,2',3,4,6	326.46							
89	2,2',3,4,6'	326.46							
90	2,2',3,4',5	326.46							
91	2,2',3,4',6	326.46							
92	2,2',3,5,5'	326.46							
93	2,2',3,5,6	326.46							
94	2,2',3,5,6'	326.46	0.00109	0.0035 0.00434	0.01 0.0156	0.0306 0.0306	0.0986 0.3103	6.4 6	35.48 13.98
95	2,2',3,5',6	326.46							
96	2,2',3,6,6'	326.46							
97	2,2',3',4,5	326.46							
98	2,2',3',4,6	326.46							
99	2,2',4,4',5	326.46							
100	2,2',4,4',6	326.46							
101	2,2',4,5,5'	326.46							
102	2,2',4,5,6'	326.46							
103	2,2',4,5,6'	326.46							
104	2,2',4,6,6'	326.46	0.004	0.004	0.004	0.004	0.004	6.3	
105	2,3,3',4,4'	326.46							
106	2,3,3',4,5	326.46							
107	2,3,3',4',5	326.46							
108	2,3,3',4,5'	326.46							
109	2,3,3',4,6	326.46							
110	2,3,3',4',6	326.46							
111	2,3,3',5,5'	326.46							
112	2,3,3',5,6	326.46							

Table 2-3 Summary of Physical-Chemical Properties of PCB Congeners (Continued)

			Solid Vapor Pressure	Subcooled Liquid Vapor Pressure	Water Solubility	Solid Molar Concentration	Subcooled Liquid Concentration	Log K _{ow}	Henry's Law Const.		
Number	Structure	Molecular Weight	P ^s Pa	P _L Pa	S g/m ³	C ^s mmol/m ³	C _L mmol/m ³		H Pa m ³ /mol		
113	2,3,3',5',6	326.46	0.0000198	0.00034	0.008	0.0145	0.233	6.3	11.91		
114	2,3,4,4',5	326.46									
115	2,3,4,4',6	326.46									
116	2,3,4,5,6	326.46									
117	2,3,4',5,6	326.46									
118	2,3',4,4',5	326.46									
119	2,3',4,4',6	326.46									
120	2,3',4,5,5'	326.46									
121	2,3',4,5',6	326.46									
122	2,3,3',4,5	326.46									
123	2',3,4,4',5	326.46									
124	2',3,4,5,5'	326.46									
125	2',3,4,5,6'	326.46									
126	3,3',4,4',5	326.46									
127	3,3',4,5,5'	326.46									
128	2,2',3,3',4,4'	360.91			0.0006	0.00166	0.0286	7			
129	2,2',3,3',4,5	360.91			0.0006	0.00166	0.0065	7.3			
130	2,2',3,3',4,5'	360.91			0.0004	0.00111	0.0061	7.3			
131	2,2',3,3',4,6	360.91									
132	2,2',3,3',4,6'	360.91									
133	2,2',3,3',5,5'	360.91									
134	2,2',3,3',5,6	360.91									
135	2,2',3,3',5,6'	360.91									
136	2,2',3,3',6,6'	360.91			0.0008	0.00222	0.0161	6.7			
137	2,2',3,4,4',5	360.91									
138	2,2',3,4,4',5'	360.91									
139	2,2',3,4,4',5'	360.91									
140	2,2',3,4,4',6'	360.91									
141	2,2',3,4,5,5'	360.91									

Table 2-3 Summary of Physical-Chemical Properties of PCB Congeners (Continued)

Number	Structure	Molecular Weight	Solid Vapor Pressure P^s Pa	Subcooled Liquid Vapor Pressure P_L Pa	Water Solubility S g/m ³	Solid Molar Concentration C^s mmol/m ³	Subcooled Liquid Concentration C_L mmol/m ³	Log K_{ow}	Henry's Law Const. H Pa m ³ /mol
142	2,2',3,4,5,6	360.91	0.000119	0.0007	0.001	0.00277	0.0163	6.9	42.9
143	2,2',3,4,5,6	360.91							
144	2,2',3,4,5',6	360.91							
145	2,2',3,4,5',6	360.91							
146	2,2',3,4',5,5'	360.91							
147	2,2',3,4,6,6'	360.91							
148	2,2',3,4',5,6'	360.91							
149	2,2',3,4',5',6	360.91							
150	2,2',3,4',6,6'	360.91							
151	2,2',3,5,5',6	360.91							
152	2,2',3,5,6,6'	360.91	0.00048	0.00363	0.002	0.0055	0.042	7	86.616
153	2,2',4,4',5,5'	360.91							
154	2,2',4,4',5,6'	360.91							
155	2,2',4,4',6,6'	360.91							
156	2,3,3',4,4',5	360.91							
157	2,3,3',4,4',5'	360.91							
158	2,3,3',4,4',6	360.91							
159	2,3,3',4,5,5'	360.91							
160	2,3,3',4,5,6	360.91							
161	2,3,3',4,5',6	360.91							
162	2,3,3',4',5,5'	360.91							
163	2,3,3',4',5,6	360.91							
164	2,3,3',4',5',6	360.91							
165	2,3,3',5,5',6	360.91							
166	2,3,4,4',5,6	360.91							
167	2,3',4,4',5,5	360.91							
168	2,3',4,4',5',6	360.91							
169	3,3',4,4',5,5'	360.91							
170	2,2',3,3',4,4',5	395.36							

Table 2-3 Summary of Physical-Chemical Properties of PCB Congeners (Continued)

			Solid Vapor Pressure P ^s Pa	Subcooled Liquid Vapor Pressure P _L Pa	Water Solubility S g/m ³	Solid Molar Concentration C ^s mmol/m ³	Subcooled Liquid Concentration C _L mmol/m ³	Log K _{ow}	Henry's Law Const. H Pa m ³ /mol	
Number	Structure	Molecular Weight								
171	2,2',3,3',4,4',6	395.36	0.0000273	0.00025	0.002	0.00506	0.046	6.7	5.4	
172	2,2',3,3',4,5,5'	395.36								
173	2,2',3,3',4,5,6	395.36								
174	2,2',3,3',4,5,6'	395.36								
175	2,2',3,3',4,5',6	395.36								
176	2,2',3,3',4,6,6'	395.36								
177	2,2',3,3',4',5,6	395.36								
178	2,2',3,3',5,5',6	395.36								
179	2,2',3,3',5,6,6'	395.36								
180	2,2',3,4,4',5,5'	395.36								
181	2,2',3,4,4',5,5'	395.36								
182	2,2',3,4,4',5,6'	395.36								
183	2,2',3,4,4',5',6	395.36								
184	2,2',3,4,4',6,6'	395.36								
185	2,2',3,4,5,5',6	395.36	0.00045	0.00114	0.0191	7	7.4			
186	2,2',3,4,5,6,6'	395.36								
187	2,2',3,4',5,5',6	395.36								
188	2,2',3,4',5,6,6'	395.36								
189	2,3,3',4,4',5,5'	395.36								
190	2,3,3',4,4',5,6	395.36								
191	2,3,3',4,4',5',6	395.36								
192	2,3,3',4,5,5',6	395.36								
193	2,3,3',4',5,5',6	395.36								
194	2,2',3,3',4,4',5,5'	429.81			0.0002	0.00047		0.0098		
195	2,2',3,3',4,4',5,6	429.81								
196	2,2',3,3',4,4',5',6	429.81								
197	2,2',3,3',4,4',6,6'	429.81								
198	2,2',3,3',4,5,5',6	429.81								
199	2,2',3,3',4,5,5',6'	429.81								

Table 2-3 Summary of Physical-Chemical Properties of PCB Congeners (Continued)

Number	Structure	Molecular Weight	Solid Vapor Pressure P^s Pa	Subcooled Liquid Vapor Pressure P_L Pa	Water Solubility S g/m^3	Solid Molar Concentration C^s $mmol/m^3$	Subcooled Liquid Concentration C_L $mmol/m^3$	Log K_{ow}	Henry's Law Const. H $Pa\ m^3/mol$
200	2,2',3,3',4,5,6,6'	429.81	0.0000266	0.0006	0.0003	0.0007	0.0158	7.1	38.08
201	2,2',3,3',4,5',6,6'	429.81							
202	2,2',3,3',5,5',6,6'	429.81							
203	2,2',3,4,4',5,5',6	429.81							
204	2,2',3,4,4',5',6,6'	429.81							
205	2,3,3',4,4',5,5',6	429.81	0.000000197	0.000012	0.00011	0.000237	0.0146	7.2	82.2
206	2,2',3,3',4,4',5,5',6	464.26							
207	2,2',3,3',4,4',5,6,6'	464.26							
208	2,2',3,3',4,5,5',6,6'	464.26							
209	2,2',3,3',4,4',5,5',6,6'	498.71	5.02E-08	0.00003	0.000001	0.000002	0.0144	8.26	20.84

Table 2-4 Summary of Physical-Chemical Properties of PCB Isomer Groups and Aroclor Mixtures at 20-25 Degrees Celsius

PCB Isomer Groups	Water Solubility S g/m ³	Solid Molar Concentration C ^s mmol/m ³	Subcooled Liquid Concentration C _L mmol/m ³	Solid Vapor Pressure P ^s Pa	Subcooled Liquid Vapor Pressure P _L Pa	Henry's Law Const. H Pa m ³ /mol	Log K _{ow} range
Biphenyl	7.0	45.39	129.7	1.30	3.69	28.64	3.90
Mono-	1.21 - 5.50	6.36 - 29.15	113.24 - 35.66	0.271 - 2.04	0.9 - 2.5	42.56 - 75.55	4.3 - 4.60
Di-	0.060 - 2.0	0.269 - 8.96	4.56 - 10.14	0.0048 - 0.279	0.008 - 0.60	17.0 - 92.21	4.9 - 5.30
Tri-	0.015 - 0.40	0.0582 - 1.55	0.24 - 2.39	0.0136 - 0.143	0.003 - 0.22	24.29 - 92.21	5.5 - 5.90
Tetra-	0.0043 - 0.010	0.0147 - 0.342	0.133 - 1.30	0.000059 - 0.0054	0.002	1.72 - 47.59	5.6 - 6.50
Penta-	0.004 - 0.020	0.0123 - 0.0613	0.093 - 0.337	0.000304 - 0.0093	0.0023 - 0.051	24.8 - 151.4	6.2 - 6.50
Hexa-	0.0004 - 0.0007	0.0011 - 0.002	0.0061 - 0.0286	0.000020 - 0.0015	0.0007 - 0.012	11.9 - 818	6.7 - 7.30
Hepta-	0.000045 - 0.0002	0.00114 - 0.0051	0.0191 - 0.046	0.0000273	0.00025	5.40	6.7 - 7.0
Octa-	0.0002 - 0.0003	0.00047 - 0.0007	0.0098 - 0.0158	0.0000266	0.0006	38.08	7.10
Nona-	0.00018 - 0.0012	0.000038 - 0.00024	0.00141 - 0.0146				7.2 - 8.16
Deca-	0.000761	0.0000024	0.0144	0.00000005	0.00003	20.84	8.26

Aroclor Mixtures	Water Solubility S g/m ³		Subcooled Liquid Concentration C _L mmol/m ³		Subcooled Liquid Vapor Pressure P _L Pa	Henry's Law Const. H Pa m ³ /mol	Log K _{ow} range
Aroclor 1016	0.22 - 0.84		0.856 - 0.216		0.06 - 0.2	70 - 900	4.4 - 5.8
Aroclor 1221	0.59 - 5.0		0.307 - 26.0		0.89 - 2.0	34 - 450	4.1 - 4.7
Aroclor 1232	1.45		6.56 - 2.0		0.54	82 - 270	4.5 - 5.2
Aroclor 1242	0.1 - 0.75		0.383 - 2.87		0.05 - 0.13	45 - 130	4.5 - 5.8
Aroclor 1248	0.1 - 0.5		0.347 - 1.74		0.0085 - 0.11	5 - 300	5.8 - 6.3
Aroclor 1254	0.01 - 0.30		0.306 - 0.92		0.008 - 0.02	20 - 260	6.1 - 6.8
Aroclor 1260	0.003 - 0.08		0.00806 - 0.215		0.0002 - 0.012	20 - 60	6.3 - 7.5

Table 2-5 Molecular Composition of Some Aroclors
(from Huntzinger *et al.*, 1974)

Chlorobiphenyl Composition	Presence (%) in Aroclor			
	1242	1248	1254	1260
C ₁₂ H ₉ Cl	3			
C ₁₂ H ₈ Cl ₂	13	2		
C ₁₂ H ₇ Cl ₃	28	18		
C ₁₂ H ₆ Cl ₄	30	40	11	
C ₁₂ H ₅ Cl ₅	22	36	49	12
C ₁₂ H ₄ Cl ₆	4	4	34	38
C ₁₂ H ₃ Cl ₇			6	41
C ₁₂ H ₂ Cl ₈				8
C ₁₂ HCl ₉				1

Table 2-6 (from Schulz *et al.*, 1989) and Figure 2-2 present the congener composition (on a weight basis) of Aroclor 1242. From this table, it can be seen that the most abundant congener in this Aroclor is 2,4'-dichlorobiphenyl (PCB 8) at 7.65% by weight. The congeners 2,4,4'-trichlorobiphenyl (PCB 28) and 2,2',5-trichlorobiphenyl (PCB 18) are also abundant at 6.52% and 6.28% by weight, respectively.

A large number of studies have linked PCBs with a variety of health effects, including cancer. A study of four commercial mixtures (Aroclors 1016, 1242, 1254, and 1260) demonstrated that all PCB mixtures can cause cancer, although different mixtures have different potencies (Brunner *et al.*, 1996). The EPA used the study by Brunner *et al.* (1996) to develop cancer slope factors for different congeners (EPA, 1996). The cancer slope factors also vary depending on the route of exposure. Table 2-7 presents the cancer slope factors for different PCB aroclors and exposure pathways.

There is evidence that dioxin-like congeners may cause cancer by the same mechanism as 2,3,7,8 tetrachlorodibenzo-p-dioxin (dioxin). EPA (1996) has developed toxicity equivalency factors that allow the toxicity of dioxin-like congeners to be related to the toxicity of dioxin. Table 2-7 presents the cancer slope factors for specific congeners based on their similarity to dioxin. Congeners 77 (34-34), 126 (345-34) and 169 (345-345) are non-ortho chlorinated and most resemble dioxin (Sonzogni *et al.*, 1991). These congeners have the highest cancer slope factors. The congeners with the most dioxin-like behavior have chlorine molecules in non-ortho positions. This is significant because PCBs with chlorines in non-ortho positions are the most suitable to anaerobic dechlorination, as discussed in detail later in this paper. The Aroclors and congeners presented in Table 2-7 are those evaluated in the human health risk assessment for the Lower Fox River and Green Bay.

Table 2-6 Percent Contribution of Individual Congeners to Aroclor 1242

Number	Structure	Weight Percent
0 0		0
1 2		0
2 3		0
3 4		0
4 2,2'		3.01
5 2,3		0.060
6 2,3'		1.38
7 2,4		0.60
8 2,4'		7.65
9 2,5		0.54
10 2,6		0.20
11 3,3'		0
12 3,4		0
13 3,4'		0
14 3,5		0
15 4,4'		1.51
16 2,2',3		2.01
17 2,2',4		2.88
18 2,2',5		6.28
19 2,2',6		0.53
20 2,3,3'		0.29
21 2,3,4		0
22 2,3,4'		3.41
23 2,3,5		0.00
24 2,3,6		0.22
25 2,3',4		0.79
26 2,3',5		1.33
27 2,3',6		0.28
28 2,4,4'		6.52
29 2,4,5		0.10
30 2,4,6		0
31 2,4',5		4.59
32 2,4',6		0.88
33 2,3,4		4.79
34 2',3,5		0.050
35 3,3',4		0.11
36 3,3',5		0
37 3,4,4'		0.27
38 3,4,5		0
39 3,4',5		0
40 2,2',3,3'		0.89
41 2,2',3,4		1.86
42 2,2',3,4'		0.83
43 2,2',3,5		0
44 2,2',3,5'		3.20
45 2,2',3,6		1.16
46 2,2',3,6'		0.49
47 2,2',4,4'		0.94
48 2,2',4,5		0.82
49 2,2',4,5'		3.60
50 2,2',4,6		0
51 2,2',4,6'		0.23
52 2,2',5,5'		4.04

Number	Structure	Weight Percent
53 2,2,5,6'		0.64
54 2,2',5,6'		0
55 2,3,3',4		0
56 2,3,3',4'		1.60
57 2,3,3',5		0
58 2,3,3',5'		0
59 2,3,3',6		0.34
60 2,3,4,4'		1.33
61 2,3,4,5		0
62 2,3,4,6		0
63 2,3,4',5		0.23
64 2,3,4',6		1.64
65 2,3',4,4'		0
66 2,3',4,4'		1.66
67 2,3',4,5		0.41
68 2,3',4,5'		0
69 2,3',4,6		0.11
70 2,3',4',5		3.89
71 2,3',4',6		0
72 2,3',5,5'		0
73 2,3',5',6		0
74 2,4,4',5		2.17
75 2,4,4',6		0.11
76 2',3,4,5		0
77 3,3',4,4'		0.45
78 3,3',4,5		0
79 3,3',4,5'		0
80 3,3',5,5'		0
81 3,4,4',5		0
82 2,2',3,3',4		0.44
83 2,2',3,3',5		0.12
84 2,2',3,3',6		0.72
85 2,2',3,4,4'		0.53
86 2,2',3,4,5		0
87 2,2',3,4,5'		0.77
88 2,2',3,4,6		0
89 2,2',3,4,6'		0
90 2,2',3,4',5		0.32
91 2,2',3,4',6		0.17
92 2,2',3,5,5'		0.25
93 2,2',3,5,6		0
94 2,2',3,5,6'		0
95 2,2',3,5',6		2.87
96 2,2',3,6,6'		0
97 2,2',3',4,5		0.65
98 2,2',3',4,6		0
99 2,2',4,4',5		0.86
100 2,2',4,4',6		0
101 2,2',4,5,5'		1.33
102 2,2',4,5,6'		0
103 2,2',4,5,6'		0
104 2,2',4,6,6'		0

Table 2-6 Percent Contribution of Individual Congeners to Aroclor 1242 (Con't)

Number	Structure	Weight Percent
105	2,3,3',4,4'	0.86
106	2,3,3',4,5	0
107	2,3,3',4',5	0.07
108	2,3,3',4,5'	0
109	2,3,3',4,6	0
110	2,3,3',4',6	1.53
111	2,3,3',5,5'	0
112	2,3,3',5,6	0
113	2,3,3',5',6	0
114	2,3,4,4',5	0
115	2,3,4,4',6	0
116	2,3,4,5,6	0
117	2,3,4',5,6	0
118	2,3',4,4',5	1.62
119	2,3',4,4',6	0.05
120	2,3',4,5,5'	0
121	2,3',4,5',6	0
122	2,3,3',4,5	0
123	2',3,4,4',5	0
124	2',3,4,5,5'	0
125	2',3,4,5,6'	0
126	3,3',4,4',5	0
127	3,3',4,5,5'	0
128	2,2',3,3',4,4'	0
129	2,2',3,3',4,5	0
130	2,2',3,3',4,5'	0
131	2,2',3,3',4,6	0
132	2,2',3,3',4,6'	0.30
133	2,2',3,3',5,5'	0
134	2,2',3,3',5,6	0
135	2,2',3,3',5,6'	0.08
136	2,2',3,3',6,6'	0.07
137	2,2',3,4,4',5	0
138	2,2',3,4,4',5'	0.54
139	2,2',3,4,4',5'	0
140	2,2',3,4,4',6'	0
141	2,2',3,4,5,5'	0
142	2,2',3,4,5,6	0
143	2,2',3,4,5,6	0
144	2,2',3,4,5',6	0
145	2,2',3,4,5',6	0
146	2,2',3,4',5,5'	0
147	2,2',3,4,6,6'	0
148	2,2',3,4',5,6'	0
149	2,2',3,4',5',6	0.63
150	2,2',3,4',6,6'	0
151	2,2',3,5,5',6	0
152	2,2',3,5,6,6'	0
153	2,2',4,4',5,5'	0.68
154	2,2',4,4',5,6'	0
155	2,2',4,4',6,6'	0
156	2,3,3',4,4',5	0.09

Number	Structure	Weight Percent
157	2,3,3',4,4',5'	0
158	2,3,3',4,4',6	0
159	2,3,3',4,5,5'	0
160	2,3,3',4,5,6	0
161	2,3,3',4,5',6	0
162	2,3,3',4',5,5'	0
163	2,3,3',4',5,6	0
164	2,3,3',4',5',6	0
165	2,3,3',5,5',6	0
166	2,3,4,4',5,6	0
167	2,3',4,4',5,5	0
168	2,3',4,4',5',6	0
169	3,3',4,4',5,5'	0
170	2,2',3,3',4,4',5	0.11
171	2,2',3,3',4,4',6	0.05
172	2,2',3,3',4,5,5'	0
173	2,2',3,3',4,5,6	0
174	2,2',3,3',4,5,6'	0
175	2,2',3,3',4,5',6	0
176	2,2',3,3',4,6,6'	0
177	2,2',3,3',4',5,6	0
178	2,2',3,3',5,5',6	0
179	2,2',3,3',5,6,6'	0
180	2,2',3,4,4',5,5'	0.06
181	2,2',3,4,4',5,5'	0
182	2,2',3,4,4',5,6'	0
183	2,2',3,4,4',5',6	0
184	2,2',3,4,4',6,6'	0
185	2,2',3,4,5,5',6	0
186	2,2',3,4,5,6,6'	0
187	2,2',3,4',5,5',6	0
188	2,2',3,4',5,6,6'	0
189	2,3,3',4,4',5,5'	0
190	2,3,3',4,4',5,6	0
191	2,3,3',4,4',5',6	0
192	2,3,3',4,5,5',6	0
193	2,3,3',4',5,5',6	0
194	2,2',3,3',4,4',5,5'	0
195	2,2',3,3',4,4',5,6	0
196	2,2',3,3',4,4',5',6	0
197	2,2',3,3',4,4',6,6'	0
198	2,2',3,3',4,5,5',6	0
199	2,2',3,3',4,5,5',6'	0
200	2,2',3,3',4,5,6,6'	0
201	2,2',3,3',4,5',6,6'	0
202	2,2',3,3',5,5',6,6'	0
203	2,2',3,4,4',5,5',6	0
204	2,2',3,4,4',5',6,6'	0
205	2,3,3',4,4',5,5',6	0
206	2,2',3,3',4,4',5,5',6	0
207	2,2',3,3',4,4',5,6,6'	0
208	2,2',3,3',4,5,5',6,6'	0
209	2,2',3,3',4,4',5,5',6,6'	0

Figure 2-2 Percent Contribution of Individual Congeners to Aroclor 1242

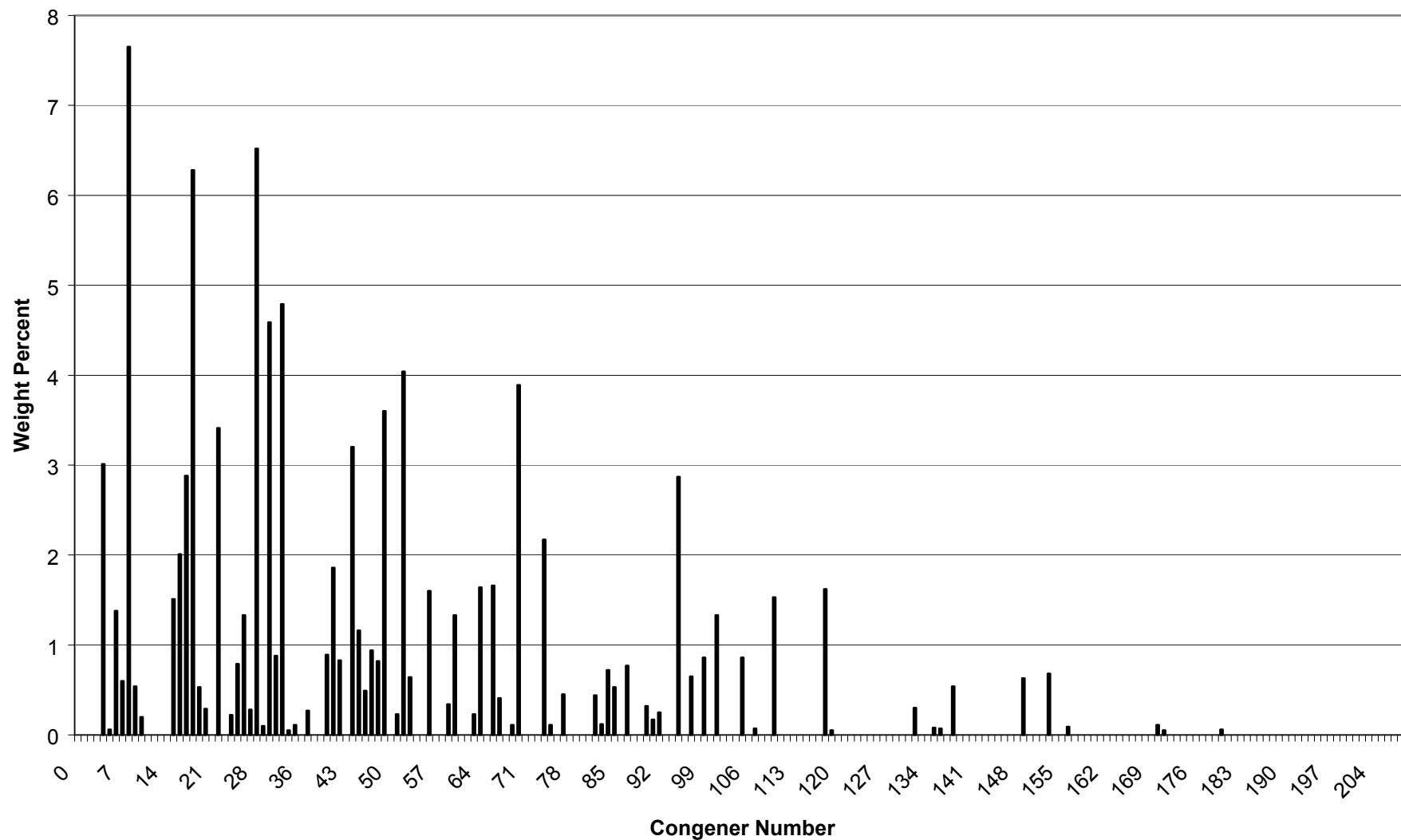


Table 2-7 Cancer Slope Factors for Selected Aroclors and PCB Congeners

Chemical of Potential Concern	Oral Soil/Sed CSFslo (mg/Kg-day) ⁻¹	Oral Water CSFwo (mg/Kg-day) ⁻¹	Oral Fish/Food CSFfo (mg/Kg-day) ⁻¹	Dermal Soil/Sed CSFsld (mg/Kg-day) ⁻¹	Dermal Water CSFwd (mg/Kg-day) ⁻¹	Inhalation Vapor CSFavi (mg/Kg-day) ⁻¹	Inhalation Particulate CSFapi (mg/Kg-day) ⁻¹
Aroclor 1016	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Aroclor 1221	2	0.4	2	2	0.4	0.4	2
Aroclor 1232	2	0.4	2	2	0.4	0.4	2
Aroclor 1242	2	0.4	2	2	0.4	0.4	2
Aroclor 1248	2	0.4	2	2	0.4	0.4	2
Aroclor 1254	2	0.4	2	2	0.4	0.4	2
Aroclor 1260	2	0.4	2	2	0.4	0.4	2
3,3',4,4'-TeCB (PCB-77)	75	75	75	75	75	75	75
2,3,3',4,4'-PeCB (PCB-105)	15	15	15	15	15	15	15
2,3,4,4',5-PeCB (PCB-114)	75	75	75	75	75	75	75
2,3',4,4',5-PeCB (PCB-118)	15	15	15	15	15	15	15
2',3,4,4',5-PeCB (PCB-123)	15	15	15	15	15	15	15
3,3',4,4',5-PeCB (PCB-126)	15,000	15,000	15,000	15,000	15,000	15,000	15,000
2,3,3',4,4',5-HxCB (PCB-156)	75	75	75	75	75	75	75
2,3,3',4,4',5'-HxCB (PCB-157)	75	75	75	75	75	75	75
2,3',4,4',5,5'-HxCB (PCB-167)	1.5	1.5	1.5	1.5	1.5	1.5	1.5
3,3',4,4',5,5'-HxCB (PCB-169)	1,500	1,500	1,500	1,500	1,500	1,500	1,500
2,2',3,3',4,4',5-HpCB (PCB-170)	15	15	15	15	15	15	15
2,2',3,4,4',5,5'-HpCB (PCB-180)	1.5	1.5	1.5	1.5	1.5	1.5	1.5
2,3,3',4,4',5,5'-HpCB (PCB-189)	15	15	15	15	15	15	15

3

Review of PCB Microbial Degradation Processes

PCBs are stable compounds that do not degrade easily. Under certain conditions, they may be destroyed by chemical, thermal, and biological processes (Erickson, 1986). In the environment, photolysis is the only significant chemical degradation process. However, microbial processes are the main route of environmental degradation in PCBs.

Photochemical degradation in water or sediments is likely not a significant means of PCB losses in the environment due to the following facts (Hutzinger *et al.*, 1974):

- PCBs have low solubilities in water; and
- UV and solar radiation do not penetrate deeply into solid media, making photodegradation in the solid state inefficient.

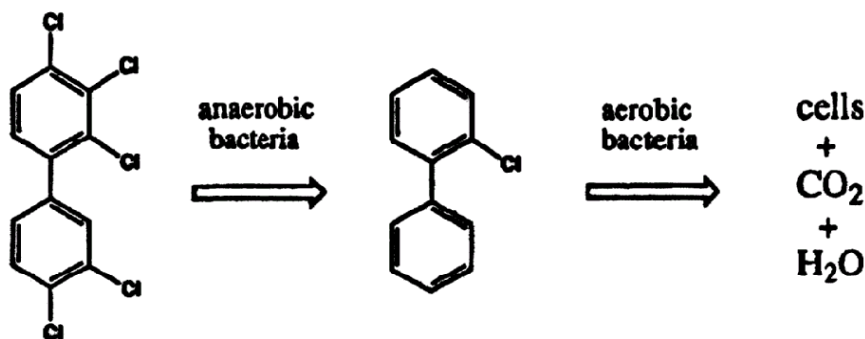
These facts also make experiments on the photodecompositions of PCBs difficult to carry out. Photodegradation in the atmosphere has been studied (see Erickson [1986] and references therein) and half lives for atmospheric photodegradation have been measured as ranging from 0.62 to 1.4 days for monochlorobiphenyls to 67 days pentachlorobiphenyls. (These data, however contradict information presented in Hutzinger, Safe *et al.* [1974] who state that “higher chlorinated biphenyls disappear faster than those with lower chlorine content on irradiation” [page 123].) Volatilization can result in significant removal of PCBs from an environmental department without any net loss of PCBs from the environment. Once volatilized, however, the chances of photodegradation are increased (Erickson, 1986).

PCBs can undergo microbial degradation in natural environments under both aerobic (i.e., in the presence of oxygen) and anaerobic (i.e., in the absence of oxygen) conditions. Under aerobic conditions, PCB congeners can be degraded by microbial processes that result in the breaking of a carbon to carbon bond of the biphenyl molecular frame, the net destruction of PCBs, and the generations of degradation by-products. Under anaerobic conditions, PCB congeners can be degraded by microbial processes that result in the substitution of chlorine atoms with hydrogen atoms within a PCB molecule. This results in the transformation of PCB congeners into other less chlorinated PCB congeners (Abramowicz, 1990). This process is referred to as dechlorination. Aerobic degradation results in a net PCB loss from a given PCB inventory, whereas anaerobic dechlorination does not.

In river sediments, aerobic conditions are typically found in the top few centimeters of the sediment core, while anaerobic conditions are found at greater depths.

Figure 3-1 (reproduced from Abramowicz [1990]) illustrates the effect of aerobic and anaerobic PCB degradation. In the first step, mediated by anaerobic bacteria, the pentachlorobiphenyl (five chlorine atoms) congener is transformed into a monochlorobiphenyl (a single chlorine atom). In the second step, mediated by aerobic bacteria, the monochlorobiphenyl is degraded to microbial cells, carbon dioxide and water.

Figure 3-1 Aerobic and Anaerobic PCB Degradation



3.1 Aerobic PCB Degradation

The microbial degradation of PCBs under aerobic conditions is well documented and studied (see for example: Abramowicz, 1990; Bedard, 1990 and references therein). Naturally occurring organisms that can degrade PCBs aerobically are quite common in nature and consist of many microbiological types. A diverse group of 25 strains of aerobic PCB-degrading bacteria has been isolated and characterized. All organisms isolated have the ability to degrade the less chlorinated PCBs, i.e., mono-, di-, some tri-, and possibly some tetrachlorinated biphenyls. However, as the number of chlorines per PCB increases, the fraction of organisms capable of degrading these congeners decreases. In particular, no aerobic microorganisms have been reported to degrade penta- and higher chlorinated PCB congeners (Abramowicz, 1990).

Furukawa (1986) reports that commercial PCB mixtures that contain predominantly mono- and dichlorobiphenyls readily undergo primary

biodegradation by activated sludge microorganisms, and that as the levels of tri-, tetra-, and pentachlorobiphenyls increase, the degradation rates decrease accordingly. Furukawa (1986) reports degradation rates in laboratory experiments ranging from > 50 nmol/ml/h for some monochlorobiphenyls to 0 for some tetrachlorobiphenyls. He indicates that PCBs containing two chlorines in the *ortho* position of a single ring (i.e., 2,6) and in each ring (i.e., 2,2') show a striking resistance to degradation. The congener 2,4,6-trichlorobiphenyl is the exception to this rule.

In reference to the molecular composition of Aroclor 1242, which is the main contaminant originally discharged in the Fox River, the data presented in Table 2-4 indicates that 76% of this Aroclor is comprised of tetra- and lower chlorobiphenyls. As such, based on the data discussed above, up to 76% of Aroclor 1242 can be degraded aerobically under the proper conditions. A greater percent might be degraded aerobically after the Aroclor has undergone some degree of dechlorination (see discussion in Section 3-2).

Even though laboratory studies have documented the existence of naturally occurring aerobic bacteria capable of degrading a large spectrum of PCB congeners, there is little direct evidence indicating that the aerobic degradation process is effective at reducing the PCB mass under field conditions. The difficulty of documenting such occurrences may explain the lack of direct observation. Another explanation may reside in the fact that a biphenyl must be present as the sole carbon source for effective PCB degradation under aerobic conditions. This may represent a major obstacle to PCB degradation *in situ*, since PCB congeners themselves apparently cannot support bacterial activity in the absence of a biphenyl substrate. No alternate substrate has been identified that is capable of sustaining or enhancing the activity of PCB-degrading bacteria under aerobic conditions (Bedard, 1990).

Of the papers reviewed, only a few addressed aerobic degradation of PCBs in sediments. Laboratory and controlled field studies (using caissons driven into the sediments to isolate them from the surrounding environment) were performed to assess the extent of aerobic biodegradation of PCBs in the Hudson River (Harkness *et al.*, 1993; Harkness *et al.*, 1994). These studies indicated that indigenous aerobic microorganisms can degrade the less chlorinated PCBs present in Hudson River sediments, and that aerobic PCB biodegradation can be stimulated by adding inorganic nutrients, biphenyl, and oxygen. Less than 60% of the PCBs in the Hudson River sediment samples that were collected in both field and laboratory experiments were biodegraded aerobically. In the laboratory studies, PCB losses were highest for mono- and dichlorobiphenyls (approximately 50% for monochlorobiphenyls and 43% - 47% for dichlorobiphenyls). Losses for trichlorobiphenyls ranged between 26% and 30%. Losses for higher chlorinated

congeners ranged between 17% and 5%. In the field studies, similar results were obtained with monochlorobiphenyl losses averaging greater than 60%, and dichlorobiphenyl losses averaging greater than 50%. Lesser losses of higher molecular congeners were also observed. Harkness *et al.* (1993) indicate that up to 90% of PCBs can potentially be degraded aerobically based on previous laboratory experiments. They state that a potential short-term biodegradation limit in both the laboratory and the field might be physically determined by the desorption kinetics of the PCBs from the sediments.

The occurrence of aerobic degradation of PCBs in Hudson River sediments is also supported by the presence of intermediate metabolites in the sediments, such as chlorobenzoic acids. A correlation between chlorobenzoic acids and PCB concentrations was demonstrated, supporting the hypothesis that these acids were formed as a by-product of the aerobic degradation of PCBs (Flanagan and May, 1993).

Grasse River sediments were demonstrated to contain microorganisms that can aerobically degrade the lower chlorinated congeners in Aroclor 1242 spiked sediments as the test substrate (Minkley *et al.*, 1999a; Minkley, Blough *et al.*, 1999b).

A study of PCB patterns in Green Bay sediments (PCB concentrations not exceeding 2 mg/kg) by Pham (1993) suggests that aerobic biodegradation is not a significant transformation mechanism in those sediments. Similarly, McLaughlin (1994) reports that no evidence of significant aerobic biodegradation was found in Lower Fox River sediments. A discussion of the findings of Pham (1993) and McLaughlin (1994) is provided in Sections 4.1 and 4.2.

Research in the application of bioremediation techniques for the treatment *in situ* of soils and sediments contaminated with PCBs is ongoing (see, for example, the review presented in Morris and Pritchard [1994]). Ongoing research focuses on the development of methods to improve the bioavailability of PCBs for degradation (Rogers, 1998). The engineered combination of aerobic and anaerobic biodegradation has been identified as a promising approach to remedy PCBs in soils or sediments. Laboratory comparison of reactor-based versus *in situ* PCB processes has demonstrated significantly higher rates of PCB destruction in soil slurry reactors. However, for many sites the advantages of not excavating continues to favor the *in situ* process configuration as a very viable, albeit slower, alternative (Shannon, Rothmel *et al.*, 1994).

In summary, based on the literature reviewed, aerobic bacteria have been shown to be capable of degrading the less chlorinated PCBs under laboratory conditions. In addition, aerobic biodegradation of PCBs in sediments was observed under

controlled field conditions and after the addition of amendments and oxygen. Finally, intermediate metabolites of aerobic PCB degradation were detected in one study of field sediments. However, significant intrinsic aerobic degradation has not been widely demonstrated under field conditions, nor have engineered approaches yet been discovered and implemented that would result in the effective aerobic degradation of PCBs in surface waters, soils or sediments. In particular, there is no significant evidence of longer scale natural PCB degradation occurring in sediments.

3.2 Anaerobic PCB Dechlorination

Reductive dechlorination under anaerobic conditions is generally viewed as an important means of biodegradation for numerous compounds including organochlorine pesticides (e.g., DDT, lindane), alkyl solvents (e.g., PCE, TCE, chloroform), and aryl halides (e.g., chlorobenzenes, PCBs, chlorophenols). Reductive dechlorination can alter the toxicity of these compounds and make them more readily degradable. Reductive dechlorination is mainly known to occur under anaerobic conditions, and it involves the substitution of a chlorine atom with a hydrogen atom within a PCB molecule (Mohn and Tiedje, 1992).

Starting in the mid 1980s, alterations in the composition of PCBs present in anaerobic river and lake sediments with respect to the original PCB composition have been widely documented. These alterations involve the removal of highly chlorinated PCB congeners with corresponding increases in the concentration of PCB congeners containing less chlorine substitutions (mono-, di-, and tri-dominated chlorobiphenyls). Three major patterns of alterations were observed for Hudson River sediments that were originally contaminated with Aroclor 1242. All three patterns showed lower levels of tri-, tetra-, and pentachlorobiphenyls and increased levels of mono- and dichlorobiphenyls. It was suggested that transformation processes such as evaporation or aerobic degradation could not account for the changes observed. It was, therefore, proposed that anaerobic microorganisms in the sediments were reductively dechlorinating the PCBs (Brown *et al.*, 1985; Brown, Jr. *et al.*, 1987).

The anaerobic dechlorination process is complex and diverse and can vary widely in the field, even at a scale of a few feet or less. There are at least five major factors that are of importance in determining whether or not the dechlorination of a particular chlorine on a PCB congener can occur in anaerobic sediments (Bedard and Quensen, 1995):

- 1) the nature of the active microbial population(s);
- 2) the type of chlorine substitution to be removed (*ortho*, *meta* or *para*);
- 3) the surrounding chlorine configuration on the phenyl ring;

- 4) the chlorine configuration on the opposite phenyl ring; and
- 5) the incubation conditions (temperature, redox conditions, ionic strength, type of carbon substrate, availability of electron acceptors, presence of oil, presence of other contaminants, etc.).

Anaerobic dechlorination of PCBs occurs via a set of specific, microbially mediated, reactions. A specific set of reactions is referred to as a dechlorination process. Depending on site- and chemical-specific conditions, one or more processes may control the overall PCB dechlorination rate. A number of individual dechlorination processes have been identified in sediments at different sites. The characteristics of these dechlorination processes, and the conditions and locations where they have been observed, are presented in Bedard and Quensen (1995). A discussion of these processes is provided below.

Bedard and Quensen (1995) identified at least six separable processes that dechlorinate Aroclors. These processes are labeled M, Q, H, H', N and P. These processes can occur alone or in combinations. For example, a dechlorination pattern, labeled C, has been identified that is the combination of processes M and Q, which are mediated by different microorganisms. Also, processes M and/or H and H' have been shown to occur concurrently at some sites. The processes can be distinguished by their congener selectivity patterns and by their chlorophenyl group reactivity patterns. Figure 3-2 (reproduced from Bedard and Quensen [1995]) provides, as an example, the dechlorination patterns for Process N.

Table 3-1 (reproduced from Bedard and Quensen [1995]) presents a summary of the chlorophenyl reactivity patterns of the various PCB dechlorination processes.

Table 3-2 (reproduced from Bedard and Quensen [1995]) summarizes the characteristics of the PCB dechlorination processes.

None of the processes described by Bedard and Quensen (1995) have been shown to remove chlorine in the *ortho* substitution. The dechlorination of *ortho*-substituted chlorine has, however, been reported to occur (albeit less prevalently than other types of dechlorination) both in the laboratory and the field (Brown, Jr. *et al.*, 1987; Minkley, *et al.* 1999a; Minkley *et al.*, 1999b).

Anaerobic dechlorination of Aroclor 1248–spiked sediments in an anaerobic bioreactor has been demonstrated by Pagano, Scrudato *et al.* (1995). The bioreactor was operated in a batch recycle mode and sanitary landfill leachate was used as a carbon, nutrient and/or microbial source. Research in this area is ongoing.

Figure 3-2 Dechlorination Process N

DECHLORINATION PROCESS N			
		234-4	→ 24-4
		236-4	→ 26-4
		245-4	→ 24-4
		25-34	→ 25-4
	234-34	→ 24-34	→ 24-4
	245-34	→ 24-34	→ 24-4
	236-34	→ 26-34	→ 26-4
	234-25	→ 24-25	
	245-25	→ 24-25	
	236-25	→ 25-26	
	234-236	→ 236-24	→ 24-26
	236-245	→ 236-24	→ 24-26
	234-234	→ 234-24	→ 24-24
2345-234	→ 234-245	→ 245-24	→ 24-24
2356-234	→ 2356-24	→ 236-24	→ 24-26
2345-2345	→ 2345-245	→ 245-245	→ 245-24
2345-2346	→ 2345-246	→ 245-246	→ 246-25
2345-2356	→ 2356-245	→ 2356-24	→ 236-24
			→ 24-26
Specificity:	Flanked meta Cl, doubly flanked meta Cl		
Reactive Groups:	34, 234, 236, 245, 2345, 2346, 23456		
	Weak activity against 235, 2356		
Unreactive meta Cl:	3, 23, 25		
Comments:	Very reactive on all tetra- through octa-CB with susceptible CP groups		
Aroclor	Reported As	Source	Reference
1260	N	Silver Lake	Quensen et al., 1990, Tab 3, Fig 8
1260	-	Silver Lake	Alder et al., 1993, Fig 6
1260	N	Woods Pond	Bedard et al., 1993, Bedard & Van Dort, in prep.
1254	H	Hudson River	Rhee et al., 1993e, Fig 1B (biphenyl)

Table 3-1 Chlorophenyl Reactivity Patterns of Various PCB Dechlorination Processes

Dechlorination Reaction	Dechlorination Process						
	M	Q	C	H	H'	P	N
3 ^a → 0	?		X				
4 → 0		X	X				
23 → 2	X	X	X		X		
24 → 2		X	X				
25 → 2	X		X				
34 → 3		X	X	X	X	X	
34 → 4	X		X				X
234 → 2		X	X				
234 ^b → 23		?					
234 ^b → 24	X	?		X	X		X
236 → 26	X	?	X		?		X
245 → 2			X				
245 → 24	?						X
245 → 25		X	X	X	X	X	
2345 → 24	NA ^c	NA	NA				X
2345 → 235	NA	NA	NA	X	X	X	

^aIt is not clear whether the ability to remove this chlorine is due to process M or to a separate activity that sometimes occurs with process M.

^bFor process Q it is not clear which chlorine is removed first, but the ultimate product is the 2-chlorophenyl group.

^cData not available.

Table 3-2 Characteristics of PCB Dechlorination Processes

Dechlorination Process	Characteristic Dechlorination Products ^a	Susceptible Chlorines	Susceptible Aroclors	Source of Microorganisms
M	2 2-2/26 2-4 24-2 24-4 26-2	Flanked and unflanked <i>meta</i>	1242 1248? 1254?	Upper Hudson Silver Lake
Q	2 2-2/26 2-3 25-2 26-2 26-3	Flanked and unflanked <i>para</i> <i>Meta</i> of 23	1242 1248 1254	Upper Hudson
C	2 2-2/26 26-2 26-3	Flanked and unflanked <i>meta</i> and <i>para</i>	1242 1248 1254	Upper Hudson
H'	2-3 2-4 24-2 25-2 24-3 25-3 26-3 24-4/25-4 24-24 ^b 24-25 25-25 235-24 ^b 235-25 ^b 236-24 ^b 236-25 ^b	Flanked <i>para</i> <i>Meta</i> of 23, 24	1242 1248 1254 1260	Upper Hudson Lower Hudson? New Bedford
H	2-3 24-3 25-3 26-3 24-4/25-4 24-24 24-25 25-25 235-24 235-25 236-24 236-25	Flanked <i>para</i> Doubly flanked <i>meta</i>	1242 1248 1254 1260	Upper Hudson Lower Hudson New Bedford Silver Lake?
P	23-25 24-25 25-25 235-23 235-25	Flanked <i>para</i>	1254? 1260	Woods Pond Silver Lake?
N	24-4 24-24 24-25 24-26 246-24 2356-24	Flanked <i>meta</i>	1254 1260	Upper Hudson Silver Lake Woods Pond

^aProducts will vary depending on the congener composition of the PCB mixture being dechlorinated.^bProposed products from Aroclors 1254 and 1260.

4 Review of Studies of Natural Degradation in Aquatic Sediments

This section discusses laboratory and field studies aimed at studying natural degradation processes, including reductive dechlorination and aerobic biodegradation, occurring in sediments at various sites. The discussion is organized by site, and (where available) the results of both laboratory and field studies are briefly discussed. The sites for which data were reviewed are the following:

- Lower Fox River;
- Green Bay;
- Sheboygan River and Harbor
- Hudson River;
- Grasse River;
- Woods Pond;
- St. Lawrence River;
- Silver Lake;
- Acushnet Estuary;
- Other Locations, including:
 - Escambia Bay,
 - Hoosic River,
 - Waukegan Harbor,
 - Lake Ketelmeer;
 - Lake Shinji (Japan), and
 - Otonabee River-Rice Lake (Canada).

4.1 Lower Fox River

Natural degradation processes in the Lower Fox River between Little Lake Buttes des Morts and the De Pere Dam were studied by McLaughlin (1994). He examined PCB congener distributions within 173 sediment cores from deposits proximate to known historical sources of PCBs to the river (deposits A and N), and from deposits 30-40 km (19-25 mi) downstream (deposits EE, GG, and HH).

McLaughlin (1994) estimated PCBs lost to weathering based on the weight fraction enrichment of congeners believed to be resistant to their respective weathering processes (desorption, biodegradation). He reports that depletion of low molecular weight congeners relative to both Aroclor 1242 and to deposits A and N was observed in downstream Fox River sediments (deposits EE, GG, and HH). This depletion is attributed mostly to desorptive losses to the water column

taking place during sediment transport downstream, rather than aerobic biodegradation. No evidence of anaerobic dechlorination of PCBs was observed in downstream deposits EE, GG, and HH, where the maximum PCB concentration is approximately 30 mg/kg.

Volatilization is not explicitly accounted for in McLaughlin (1994). However, volatilization results in a mass loss from the water column to the atmosphere. As such, volatilization of PCB mass previously sorbed to sediment can only occur after such mass has desorbed to the water column. Therefore, the explicit quantification of mass loss to volatilization from the unit column does not affect the estimate of mass loss from sediments due to biodegradation and desorption.

The congener distribution data in deposits A and N support the conclusion that anaerobic dechlorination has occurred in these deposits, along with some physical/chemical weathering. The data suggest that dechlorinating activity is limited to sediment PCB concentrations of 30 mg/kg or greater. The overall PCB losses due to microbial degradation in deposits A and N were estimated to be approximately 10% (McLaughlin, 1994) with respect to the original inventory of PCBs deposited in the river.

It was estimated that no biodegradation losses have occurred in sediments in the Lower Fox River above the DePere Dam, and that 10% biodegradation has occurred in sediments from SMUs with a PCB concentration of 30 mg/kg or higher, resulting in an overall PCB mass loss from the river of approximately 1,600 kg. Conversely, an overall 33% desorption for all river sediments was estimated, resulting in an overall PCB mass loss from the river of approximately 15,000 kg (McLaughlin, 1998).

Another evaluation of aerobic and anaerobic degradation of PCBs in Deposit A of Little Lake Buttes des Morts is provided in Appendix D, Deposit A - PCB Biodegradation Assessment from the *Remedial Investigation/Feasibility Study Little Lake Butte des Morts Sediment Deposit A* (Blasland & Bouck Engineers, 1993). Anaerobic dechlorination (as measured by a 20% decrease of the non-orthochlorine ratio with respect to the ratio of Aroclor 1242) was observed, with the exception of one sample which exhibited significantly higher levels of dechlorination. As a result of dechlorination, levels of PCB congener 2,3',4,4',5 were shown to have decreased in almost all samples. An examination of certain aerobically biodegradable congeners (2,3; 2,4'; 2,4,4'; and 2,5,4') relative to the Aroclor 1242 standard provided no evidence of aerobic degradation. Rather, the levels of these congeners were increased as a result of dechlorination. It was concluded that either no aerobic biodegradation had taken place, or its effect was being masked by the effects of anaerobic PCB dechlorination.

In another study of dechlorination patterns in the Lower Fox River (Hollifield, *et al.* 1995), PCB-contaminated sediments were collected from the southern portion of Little Lake Butte des Morts and analyzed for their congener distribution. The results of these analyses are consistent with *in situ* dechlorination of PCBs. However, the extent of *in situ* dechlorination was less than that typically reported in the literature. It was estimated that the extent of dechlorination in these sediments ranged from 3.77% to 8.18% of total chlorine, and 10.1% to 16.9% of the *meta* and *para* chlorines relative to Aroclor 1242. The dechlorination appeared to have occurred primarily at the *meta* and *para* positions, with a preference for the *meta* position noted.

Attempts by Hollifield *et al.* (1995) to further dechlorinate Fox River sediments in the laboratory met with limited success. The range of additional dechlorination ranged from -0.65% to 6.86% on a total chlorine basis, and -0.65% to 11.2% on a *meta* and *para* chlorine basis. Furthermore, all samples displaying dechlorination in the laboratory tended to converge on a common chlorine distribution (removal of ~10% of total chlorine and ~20% of *meta* and *para* chlorines, relative to Aroclor 1242). The concentration in sediments also appeared to have an effect. Those sediments with higher PCB concentrations were observed to undergo more successful dechlorination to a greater extent (quantification of this effect is not provided in Hollifield, Park *et al.* [1995]). In addition, the data were consistent with the existence of a threshold below which dechlorination will not proceed.

In summary, a threshold of approximately 30 mg/kg appears to exist in Fox River sediments for PCB dechlorination. Below this threshold, no significant anaerobic dechlorination of PCBs is expected to occur. In addition, no significant aerobic degradation has been documented in sediments throughout the river.

4.2 Green Bay

The PCB congener patterns exhibited by PCBs in Green Bay sediments are different from the congener patterns associated with Lower Fox River sediments. The congener distribution was observed to shift from the lighter, lower chlorinated biphenyls, toward the heavier, higher chlorinated biphenyl. However, the depletion of the lighter chlorinated congeners does not show selective removal of non-*ortho*-chlorinated congeners, as would be expected if aerobic degradation were occurring. Furthermore, the shift toward higher chlorinated congeners suggests that anaerobic dechlorination is not a relevant process in the sediments in Green Bay (Pham, 1993). The latter observation is consistent with the absence of dechlorination in Lower Fox River sediments containing less than 30 mg/kg total PCBs (McLaughlin, 1994).

The concentrations of PCBs in Green Bay sediments (less than 2 mg/kg) appear to be below the levels necessary for microbial degradation to occur (McLaughlin, 1998), and the differences in congener distribution between Fox River and Green Bay sediments are attributed to chemical and physical processes such as diffusion into pore water, solubilization, and re-suspension, rather than biological processes such as aerobic degradation or anaerobic dechlorination (Pham, 1993).

4.3 Sheboygan River and Harbor

The Sheboygan River flows westward and drains into Lake Michigan at the city of Sheboygan, Wisconsin. The river is contaminated with PCBs from the mouth to about 22.6 km (14 miles) upstream (Sonzogni *et al.*, 1991). Waste hydraulic fluids containing Aroclor 1248 and Aroclor 1254 were the source of the contamination (David, 1990).

The PCB congener distribution in the Sheboygan River between the Sheboygan Falls dam and the harbor in Sheboygan (22.4 km) was studied by David (1990) and Sonzogni, Maack *et al.* (1991). The conclusions of these studies are summarized below.

- The PCB congener distribution (congeners present as well as the weight percentages of each congener) from highly contaminated sediments (PCB concentration greater than 50 mg/kg) are considerably different from the PCB congener distribution of the Aroclor 1248 and 1254 which were originally discharged at the site.
- The weight percents of the toxic congeners in these sediments were generally lower than those found in Aroclor 1248 and 1254 (the primary PCB mixtures discharged to the river), and in Aroclor 1242 and 1260. The weight percents of the most toxic congeners (77, 118, and 105) were about an order of magnitude lower than the weight percents in Aroclor 1248. The average weight percents in Sheboygan River samples were 0.02%, 0.2% and 0.04% for congeners 77, 118 and 105, respectively. This compares with 0.3%, 3.35% and 0.55% for the same congeners in Aroclor 1248.
- The enrichment of the highly contaminated sediments with lower chlorinated congeners is not easily explained by known physical-chemical partitioning or known abiotic chemical reactions. This suggests that a biotic process might be responsible for the enrichment. It is suggested in David (1990) that this process is anaerobic dechlorination.

- In sediments containing concentrations less than 50 mg/kg, the congener distributions were similar to the original Aroclors, suggesting the existence of a threshold for dechlorination of approximately 50 mg/kg.

4.4 Hudson River

PCBs were first detected in fish from the Hudson River in 1969. The principal source of PCB contamination was related to the release of Aroclors to the river and river sediments.

In 1987, Brown Jr. *et al.* (Brown, Jr., Bedard *et al.*, 1987; Brown, Jr., Wagner *et al.*, 1987) reviewed chromatograms of hundreds of sediment, water, and soil samples contaminated with PCBs to determine changes in the relative concentrations of isomers with respect to the original PCB composition. They reported that in the upper Hudson River as a whole, approximately 40 to 70 metric tons of PCBs (out of an estimated total of 134 metric tons), have been converted from tri-, tetra- and higher chlorobiphenyls to mono-, di-, and predominantly *ortho*-substituted tri-chlorobiphenyls due to reductive dechlorination. Potential changes in sediment PCB congener distribution due to desorption and volatilization were not addressed in these studies. The extent of dechlorination was more pronounced in highly contaminated sediments (i.e., >50 mg/kg) but more modest in less contaminated sediments. As part of this study, the authors found evidence of dechlorination in sediments from adjacent Silver Lake, Hoosic River, Sheboygan River, and Acushnet Estuary. The dechlorination patterns were, however, different at these locations when compared with the Hudson River. The study also reported that all of the lower chlorinated PCB congeners formed by the observed reductive dechlorination could be biodegraded by one or more of the aerobic PCB-degrading bacteria that were isolated from soils and sediments. The authors proposed the hypothesis that a two-step sequence of dechlorination followed by oxidative biodegradation might eventually achieve total PCB destruction under properly engineered conditions.

In 1997, the U.S. Environmental Protection Agency (EPA) published an analysis of *in situ* dechlorination in the Hudson River from the results of a high-resolution sediment coring program (Tams Consultants, 1997). The main conclusions of this study are as follows.

- No evidence was found of extensive dechlorination within sediments in the Hudson River.
- Anaerobic dechlorination of PCBs in the Hudson River is limited to *meta* and *para* chlorines. Based on the composition of Aroclor 1242 (the main

contaminant) no more than 26% ultimate mass loss by dechlorination is possible.

- The data suggest that other PCB destruction processes are not effective at removing PCBs from the sediments.
- Dechlorination appears to proceed, to a limited degree, dependent on the initial PCB concentration and does not continue to occur indefinitely; all sediment mass loss via dechlorination has occurred for current contamination and no further significant amelioration can be expected.
- No sediments were found which had a calculated PCB mass loss of greater than 25%.
- Below a concentration of 30 mg/kg, dechlorination mass loss did not occur predictably and was frequently 0%.
- The data verify the general persistence of PCBs in the environment.

The EPA report concluded that PCBs in the sediments of the upper Hudson River can be expected to be available for sediment-water exchange, re-suspension and biological interaction for at least 35 years and probably longer.

A number of laboratory studies were performed on sediments collected from the Hudson River (or using anaerobic microorganisms obtained from these sediments). These studies were aimed at demonstrating the effectiveness of dechlorination of PCB congeners present in these sediments (Quensen III *et al.*, 1988; Quensen III *et al.*, 1990; Morris, Mohn *et al.*, 1992; Abramowicz *et al.*, 1993; Rhee *et al.*, 1993a; Rhee *et al.*, 1993b; Sokol *et al.*, 1995; Williams, 1994). The following bullet items summarize the main findings of these laboratory studies.

- The laboratory studies consistently show that dechlorination at the *meta* and *para* positions under anaerobic conditions is readily achieved in laboratory studies. However, no significant *ortho* dechlorination was observed.
- Inocula prepared from PCB-contaminated sediments from the Hudson River can effect *meta* and *para* dechlorination of sediments spiked with mixtures of Aroclor 1242, 1248, 1254 and 1260.
- Biphenyl enrichment decreased both the rate and extent of dechlorination, and affected the dechlorination products.

- The extent and rate of dechlorination in Hudson River sediments, as well as the lag time before the onset of dechlorination activity, was consistently shown to depend on PCB concentrations. Dechlorination activity was generally determined to be directly related to PCB concentration (i.e., the greater the PCB concentration, the greater the extent of dechlorination). For example, Quensen *et al.* (1988) reported that in the 700 mg/kg PCB concentration samples, the average number of *meta* plus *para* chlorines per biphenyl decreased from an average of 1.98 to 0.31 after 16 weeks, but only decreased to 1.19 in the 140 mg/kg samples. At 14 mg/kg there was no difference between the live samples and the autoclaved controls, indicating that a threshold to dechlorination might exist at or above that concentration level. Two additional studies (Rhee *et al.* 1993a, Rhee *et al.* 1993b) also report the existence of a concentration threshold for dechlorination activity (no concentration values for this threshold were provided). The threshold level might be site- and congener-specific.

4.5 Grasse River

A stretch of the Grasse River near Massena, New York was contaminated with PCBs, primarily from the release of products containing Aroclor 1242. A comprehensive field and laboratory study of naturally occurring PCB biodegradation processes in Grasse River sediments was prepared by the Carnegie Mellon Research Institute Biotechnology Group (Minkley *et al.*, 1999a; Minkley *et al.*, 1999b). The following summarizes the results of this study.

- *In situ* PCB dechlorination is an ongoing process in Grasse River sediments.
- Dechlorination activity is dependent on PCB concentration. Dechlorination appears to be occurring in sediments having less than 10 mg/kg total PCB concentration, but the statistical evidence of dechlorination at concentrations below 7 to 10 mg/kg is less strong than at higher concentrations (i.e., the statistical confidence level is less than 95%).
- The study suggested that biphenyl detected in Grasse River sediments resulted from the dechlorination of PCB congeners and that congeners with *ortho*-substituted chlorines are being degraded. In addition, the study suggested the possibility for anaerobic biodegradation of biphenyl and PCB congeners with low chlorine substitutions.

In summary, the study concluded that the Grasse River sediments are undergoing both aerobic and anaerobic PCB biodegradation under field conditions. The rate and extent of this biodegradation have not yet been determined.

4.6 Woods Pond

Woods Pond (Lenox, Massachusetts) is a shallow impoundment on the Housatonic River located 10.5 miles downstream from Silver Lake. The pond's sediments are contaminated with hydrocarbon oil and PCBs from the release of products containing Aroclor 1260 (95%) and Aroclor 1254 (5%). The results of a core sampling study in Woods Pond indicated the following (Bedard, 1990; Van Dort and Bedard, 1991; Bedard, Bunnell *et al.*, 1996; Bedard and May, 1996; Bedard, Van Dort *et al.*, 1997; Van Dort, Smullen *et al.*, 1997).

- The PCB congener distribution in Woods Pond sediments results from dechlorination of Aroclor 1260 and Aroclor 1254 (95:5).
- All samples collected from Woods Pond showed some evidence of reductive dechlorination when compared to Aroclor 1260. The sample with the most extensive dechlorination was depleted by only 13.7% of the *meta* and *para* chlorines (3.92% for Aroclor 1260 versus 3.38%, for the most extensively dechlorinated sample). The most extensively dechlorinated samples had lost 11% to 19% (2.27% to 2.08% versus 2.57% for Aroclor 1260) of the *meta* chlorines, and 2% to 7% of the *para* chlorines (1.33% to 1.26% versus 1.35% for Aroclor 1260).
- The dechlorination process targeted most of the hexa-, hepta- and octachlorobiphenyls, and converted them into tetra- and pentachlorobiphenyls containing predominantly *ortho* and *para* chlorine substitutions. *Meta* dechlorination was favored over *para* dechlorination.
- The extent and type of dechlorination process varied considerably among samples, depending on the sample location within the pond.
- It is possible to stimulate, or “prime”, in the laboratory indigenous microorganisms in Woods Pond to effect rapid dechlorination of PCBs that have persisted in the environment for decades. This was shown to be true even in the presence of high concentrations of oil (5 mg/kg).
- Under laboratory conditions, indigenous anaerobic microorganisms from Woods Pond are capable of removing chlorine from the *ortho* position of at least one PCB congener (2, 3, 5, 6-tetrachlorobiphenyl).

4.7 St. Lawrence River

The St. Lawrence River is located along the northeast border of New York State and has been contaminated with PCBs from industrial sources. The presence of PCBs was related to the release of products containing Aroclor 1248 and to a minor extent Aroclor 1260. The results of field and laboratory studies indicated the following (Sokol *et al.*, 1994; Sokol, Bethoney *et al.*, 1998a; Sokol *et al.*, 1998b).

- Sediment cores taken on the St. Lawrence River showed evidence of *in situ* reductive dechlorination at all sites along the river where cores were collected, except for one location. The extent of dechlorination varied widely from site to site, ranging from 2% to 45% (with respect to Aroclor 1248), based on the average number of chlorines per biphenyl.
- At most sites, dechlorination resulted in the removal of *meta* and *para* chlorines. *Meta* dechlorination was favored over *para* dechlorination at most sites. There was no evidence of *ortho* dechlorination at any of the sites.
- The lack of dechlorination at the one site was not attributed to the lack of competent microorganisms, but appeared to be associated with a high level of contamination (93,000 mg/kg aluminum, 4,794 mg/kg, PAHs) that may have included non-aqueous fluids.
- Location specific sediment characteristics can significantly affect indigenous populations and thus affect the resulting dechlorination pattern and extent.
- Additional dechlorination in the laboratory of partially dechlorinated samples collected in the St. Lawrence River occurred rapidly over the first four months of incubation. Over this period of time, total chlorines per biphenyl were reduced by 22% (from 3.2 to 2.5) with respect to the field samples. With further incubation, a second phase of dechlorination ensued after 15 months, with the total number of chlorines per biphenyl decreasing slightly further from 2.5 to 2.4. After this additional dechlorination the transformation reached a plateau with no further change until the end of incubation at 39 months, indicating an endpoint. These laboratory results, when compared to the field data, suggest that *in situ* dechlorination at the site has not yet reached a plateau, although they are not able to reveal the *in situ* dechlorination rate.

- Some earlier field data indicated no correlation between the extent of dechlorination and sediment PCB concentration (Sokol *et al.*, 1994). However, more recent laboratory studies (Sokol *et al.*, 1998) indicated a clear dechlorination threshold concentration of 35 to 45 ppm total PCBs. In addition, these laboratory studies indicated that above the threshold concentration, the dechlorination rate was a function of total PCB concentration.

4.8 Silver Lake

Silver Lake is a 26-acre urban pond in Pittsfield, Massachusetts. Products containing Aroclor 1254 and Aroclor 1260 were likely used and released at different times from facilities close to the lake (Bedard and Quensen, 1995).

Brown, Jr., Bedard *et al.* (1987) and Brown, Jr., Wagner *et al.* (1987) studied the PCB congener distribution in sediment and concluded that dechlorination had altered the congener distribution pattern, that the PCB deposited in Silver Lake sediments was originally virtually all Aroclor 1260, and that PCBs in Silver Lake had undergone *ortho* as well as *meta* and *para* dechlorination. Bedard and Quensen (1995), however, questioned the finding that *ortho* dechlorination occurred in Silver Lake sediments, and indicated that the observed PCB patterns can be attributed to *meta* and *para* dechlorination of Aroclor 1254.

Quensen III *et al.*, (1990) studied the rate and pattern of dechlorination of four commercial Aroclors (1242, 1248, 1254 and 1260) by microbial cultures prepared from PCB-contaminated sediments from Silver Lake and compared then with those obtained from microbial cultures from PCB-contaminated sediments in the Hudson River. In both cases dechlorination of *meta* and *para* chlorines (ranging from 15% to 85%, with the respect to the original Aroclor) was observed. For each inoculum, the rate and extent of dechlorination tended to decrease as the degree of chlorination of the Aroclor increased. The results suggested that there are different groups of PCB-dechlorinating microorganism at the two sites, and that each group has specific characteristics for PCB-dechlorination. The issue of the existence of a potential dechlorination threshold was not examined in the Silver Lake references reviewed.

4.9 Acushnet Estuary

Congener-specific analyses of the PCBs in the Acushnet Estuary (New Bedford, Massachusetts) sediments and waters were undertaken to identify the alteration and transport processes of PCBs in a coastal marine environment. PCBs in the Acushnet Estuary are from the release of products containing Aroclor 1242 and 1254. (Brown, Jr. and Wagner, 1990). The study concluded that anaerobic

microbial processes had selectively removed non-*ortho* chlorines from most of the higher chlorinated PCB congeners. The dechlorination process occurring within the Acushnet Estuary was identified as Process H. The dechlorination process appeared to have begun near the upper end of the estuary and not have yet reached the lower portions of the estuary. In addition, the study concluded that PCBs had undergone desorption into the water column and vertical movement within the sediments (rather than remaining stratified), but there was no horizontal translation between sites.

4.10 Other Locations

Limited evidence of *in situ* dechlorination at a number of additional locations is reported in Bedard and Quensen (1995). The following summarizes information from these locations and, where available, the Aroclor type constituting the bulk of the original PCB contamination. Complete quantitative congener-specific analyses of sediment PCBs was not available for any of these locations, but the data that are available suggest that PCB dechlorination has occurred to an observable extent at the following locations:

- Escambia Bay (near the mouth of the Pensacola River, FL);
- Hudson Estuary and River (near Troy, Mechanicville, Albany and Kingston, Catskill and Poughkeepsie, NY).
- Hoosic River (North Adams, MA).
- Waukegan Harbor, IL, contaminated with Aroclor 1248.
- Lake Ketelmeer, a sedimentation area of the Rhine River in the Netherlands.
- Lake Shinji, Japan, contaminated with Kanechlor 500, a commercial PCB mixture similar to Aroclor 1254.
- Otonabee River/Rice Lake, in Petersborough, Canada

5

Conclusions

The purpose of this review was to evaluate information relating to the viability of natural biodegradation as a potential remedial action for the sediment-bound PCBs in the lower Fox River and Green Bay. Based upon the evidence presented in the literature, the following conclusions can be drawn.

- Naturally occurring reductive dechlorination processes in sediments has been documented. There are three principle lines of evidence.
 - The PCB congener distribution in sediment cores has been analyzed and compared with the distribution of the original source of PCB contamination at a number of locations. This type of analysis has shown that, under the right conditions, a reduction of the concentrations of the highly chlorinated congeners and an increase in the concentrations of the medium- to lower-chlorinated congeners (indicating that dechlorination of the highly chlorinated congeners had occurred) can be documented.
 - Laboratory experiments have been performed on sediment samples contaminated with PCBs obtained from a number of different locations. These experiments have shown the ability of anaerobic microbial populations to effect dechlorination of PCBs under laboratory conditions.
 - Anaerobic microorganisms extracted from PCB-contaminated sediments have been shown to degrade sediment samples spiked with standard Aroclors.
- Anaerobic PCB degradation under field conditions was demonstrated to have occurred at almost all the sites studied. However, the reduction in PCB concentrations through anaerobic processes is site-dependent. In the Lower Fox River, only 10% reduction could be accounted for by anaerobic processes for deposits with average PCB concentrations greater than 30 mg/kg. No PCB reductions due to anaerobic processes could be accounted for in deposits with average concentrations less than 30 mg/kg. Conversely, it was estimated that 33% of the PCB mass originally deposited in the Lower Fox River was lost due to desorption (that is, the PCBs were re-suspended in the water column). Physical loss through

desorption from sediments seems to exceed any biodegradation in the Lower Fox River environment.

- *Meta* and *para* dechlorination are most prevalent under both field and laboratory conditions. However, only limited evidence supports the occurrence of *ortho*-substituted PCB congeners under both field and laboratory conditions. The concentration of *ortho*-substituted congeners in the Aroclors deposited at any given site might represent a lower limit to the extent of dechlorination achievable at that site.
- The rate and extent of dechlorination under field and laboratory conditions appear to be influenced by the overall PCB concentration in sediments. The greater the PCB concentration, the greater the rate and extent of dechlorination.
- The most well documented of the PCB contaminated sites demonstrate that a threshold PCB concentration must exist before anaerobic dechlorination can occur. The threshold PCB concentration level is site specific. At different sites, thresholds have been shown to range from about 10 mg/kg up to about 50 mg/kg. The sediments from the Lower Fox River show a threshold of 30 mg/kg. At concentration levels below 30 mg/kg no reductions of PCBs have been documented in the Lower Fox River. Based on the available data, even if these sediments could be aerated, complete removal of PCBs by biological means might not be feasible, because the highly chlorinated congeners will not dechlorinate below the threshold values. It is possible that other active treatment options might promote dechlorination of the sediments, making the PCBs more amenable to aerobic biological destruction.
- The type, rate, and extent of dechlorination processes are influenced by a number of site-specific conditions, and can vary from sample to sample even within the same site. Based on the literature reviewed, it appears that site-specific predictions on dechlorination processes cannot be made without recourse to site-specific dechlorination studies.
- Aerobic degradation of the lower chlorinated PCB congeners (which results in the actual destruction of PCB molecules) has been documented in laboratory studies, but is poorly documented under field conditions. No field rates for aerobic PCB degradation have been measured at any sites. In particular, aerobic degradation has not been documented in the Lower Fox River and Green Bay. Aerobic processes might be effective in reducing PCB concentrations if used under controlled conditions (such as sediment management units).

- Aerobic degradation is not effective at degrading the higher chlorinated PCB congeners.
- Rates of PCB destruction are not available from field studies. These rates are critical to understanding whether natural biological processes can be relied on to eventually cleanup the sediments. One of the conclusions of the EPA study of the Hudson River is that unless action is taken, PCBs in the Hudson River can be expected to be available for sediment water exchange, re-suspension, and biological interaction for at least 35 years and, possibly longer.

6

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